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certain difficulties (discussed by Sommerfeld in his book) that we encounter, if we suppose that the orbits all lie in the same plane. Possibly these difficulties will disappear, when we study more thoroughly atomic models in which the orbits do not lie in the same plane.

<sup>1</sup> E. Wagner, *Ann. Physik, Leipzig*, March, 1915 (868).

<sup>2</sup> M. de Broglie, *J. Physique, Paris*, May-June, 1916 (161); and *Paris C. R. Acad. Sci.*, Nov. 24, 1919 (962).

<sup>3</sup> Blake and Duane, *Physic. Rev., Ithaca*, Dec., 1917 (624); and Duane and Patterson, *Ibid.*, 1920.

<sup>4</sup> Siegbahn and Friman, *Phil. Mag., London*, April, 1916 (423); and Nov., 1916 (497).

<sup>5</sup> D. L. Webster, *Proc. Nat. Acad. Sci., Washington, D. C.*, Jan., 1920 (26).

<sup>6</sup> Duane and Hu, *Physic. Rev.*, June, 1918 (488); and Dec., 1919 (516); and Duane and Shimizu, *Ibid.*, Feb., 1919 (159) and Dec., 1919 (522).

<sup>7</sup> Duane and Shimizu, *Ibid.*, July, 1919 (67); Duane and Patterson, *Ibid.*, 1920; Duane and Stenström, *Ibid.*, April, 1920 (302); and *Proc. Nat. Acad. Sci.*, Aug. 1902.

<sup>8</sup> Stenström, *Doctor's Dissertation*, Lund, 1919.

<sup>9</sup> Webster and Clark, *Proc. Nat. Acad.*, March, 1917 (181).

<sup>10</sup> Rubinowicz, *Physik. Zs., Leipzig*, **19**, 1918 (441-465).

<sup>11</sup> Bohr, *Copenhagen Academy*, 1918.

<sup>12</sup> Compare Sommerfeld, *Atombau und Spektrallinien*, Chapter 6.

<sup>13</sup> Compare de Broglie *Paris, C. R. Acad. Sci.*, Nov. 24, 1919 (962).

## ON THE RELATIVE POSITIONS AND INTENSITIES OF LINES IN X-RAY SPECTRA

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*Grouping of L Series Lines.*—The wave-lengths of the lines in the *L* series of X-rays have been measured for a great many of the chemical elements by Siegbahn and Friman.<sup>1</sup> They have published graphs which represent the square roots of the frequencies of corresponding lines in the spectra of different elements as functions of the atomic number. The graphs for the lines  $1$ ,  $\alpha_2$ ,  $\alpha_1$ ,  $\beta_2$  and  $\beta_5$  are very nearly straight, indicating that the square roots of the corresponding frequencies are almost linear functions of the atomic numbers, whereas the graphs for the other lines are curved, indicating a marked departure from the linear law. This would seem to mean that we can divide the lines in the *L* series into at least two groups.

In his work on characteristic absorption de Broglie<sup>2</sup> found three critical absorption wave-lengths associated with the *L* series of gold, bismuth, thorium and uranium. The authors<sup>3</sup> have extended this, and have measured the third critical absorption wave-length as well as the other two for the elements they examined from tungsten to uranium both inclusive. The fact that three critical absorption wave-lengths appear in the *L* series of

each chemical element would seem to indicate the existence of at least three distinct groups of lines.

The researches of D. L. Webster and Harry Clark<sup>4</sup> on the voltages required to produce the various lines in the  $L$  series of platinum and on the way in which their intensities increase with increasing voltage confirm this, and prove further that the lines  $\eta$ ,  $\beta_1$ ,  $\gamma_1$  and probably  $\gamma_2$  belong to the second group.

The modern theory of line spectra, also, seems to indicate the splitting up of the  $L$  series into groups. The differences in frequency between certain lines in the first group and corresponding lines in the second group are very nearly equal to each other. These pairs of lines with nearly the same frequency interval are  $\eta-1$ ,  $\beta_1-\alpha_2$ ,  $\gamma_1-\beta_2$  and  $\gamma_2-\beta_3$ . Sommerfeld<sup>5</sup> explains this division of the  $L$  series into groups with a constant frequency difference on the assumption that one group of lines is due to electrons falling into an  $L$  orbit that is circular, and that the other group is produced by electrons falling into an  $L$  orbit that is elliptic. The equation he derives from his theory for the magnitude of the frequency difference fits the facts with considerable precision.

The following facts indicate that the critical absorption  $La_1$  belongs to the first group of lines, and that the critical absorption  $La_2$  belongs to the second group of lines. Firstly, the wave-length of the critical absorption  $La_1$  lies not far from that of the line of shortest wave-length in the first group, and the wave-length of  $La_2$  lies close to that of the line of shortest wave-length in the second group. Secondly, as the authors have shown,<sup>3</sup> the square root of the frequency of  $La_1$  for the different elements is almost a linear function of the atomic number, while that of  $La_2$  departs from the linear law in the same way as do those of the second group of lines in Siegbahn and Friman's graphs. Thirdly, the frequency difference between  $La_2$  and  $La_1$  equals to a high degree of precision that between the pairs of lines  $\eta-1$ ,  $\beta_1-\alpha_2$  and  $\gamma_2-\beta_3$  which were all measured by the authors<sup>6</sup> under the same experimental conditions for the tungsten spectrum. Fourthly, the frequency differences between  $La_2$  and  $La_1$  for the various chemical elements from tungsten to uranium<sup>3</sup> agree very well with Sommerfeld's formula. Fifthly, the values of the critical voltages of two of the groups of lines in the  $L$  series of platinum measured by Webster and Clark<sup>4</sup> (namely, 13.20 kilovolts and 11.45 kilovolts) agree very well with the values of the same quantities calculated by the quantum equation from our critical absorption wave-lengths (namely 13.26 kilovolts and 11.54 kilovolts).

*Relative Position of Lines.*—It has been shown by Duane and Hu<sup>7</sup> that the critical absorption wave-length associated with the  $K$  series of Rhodium is about one-third of a per cent shorter than that of the shortest line (the  $\gamma$  line) in that  $K$  series. Further, Duane and Stenström<sup>8</sup> have found that the difference between the wave-length of the critical absorption in

the  $K$  series of tungsten and that of its  $\gamma$  line amounts to about one-half of one per cent, the  $\gamma$  line having the longer wave-length. In the case of each element the wave-lengths were measured under exactly the same experimental conditions, so that there can be no doubt but that the critical absorption wave-length in the  $K$  series is shorter than the wave-length of the  $\gamma$  line by an amount that considerably exceeds the errors of experiment.

Turning to the  $L$  series we find that the third critical absorption wave-length,  $La_3$ , appears to be shorter than that of the line of shortest wave-length in the  $L$  series, namely,  $\gamma_4$ .<sup>3</sup> The authors<sup>6</sup> have found the following values for these wave-lengths,  $La_3 = 1.024 \pm 3$  and  $\gamma_4 = 1.0261 \pm 6$ , in the spectrum of tungsten. In the other two groups, however, the critical absorption wave-lengths are longer than those of the shortest wave-length lines respectively. In the tungsten spectrum the authors<sup>3,6</sup> found for the wave-lengths in the first group  $La_1 = 1.2136 \pm 1$  and  $\beta_5 = 1.2040 \pm 7$ , and in the second  $La_2 = 1.0726 \pm 5$  and  $\gamma_2 = 1.0655 \pm 4$ . In each case the difference between the two wave-lengths considerably exceeds the estimated errors of experiment.

As the relative position of these emission and absorption lines appears to be a matter of considerable theoretical importance the authors have repeated their experiments in a slightly different form. To make doubly sure of the facts they have taken the readings so as to show the position of the critical absorption and those of the emission lines on each side of it on one and the same curve. The experimental conditions were exactly the same as those in the experiments described in the article referred to,<sup>6</sup> except that the X-ray tube was turned so that the rays left the target making a slightly smaller angle with its surface than in the earlier experiments. This increased the absorption of the rays by the target itself, and made the absorption drop in the curves more prominent.

The curve in figure 1 represents the intensity of the radiation (measured by the currents in the X-ray spectrometer's ionization chamber) as a function of the crystal table angles. The drop in the curve marked  $a_1$  corresponds to the critical absorption belonging to the first group of  $L$  series emission lines. The absorption of its own rays by the tungsten target alone produced this drop, as no absorbing screen was introduced in the path of the rays in this experiment. The tall peak on the curve represents the relatively strong emission line  $\beta_2$ . Its separation from the absorption drop corresponds very well with the wave-length interval between the two, calculated from the data obtained in the earlier experiments, namely  $0.0283 \pm 2$ . The small hump in the curve on the other side of the absorption drop represents the emission line,  $\beta_5$ .

This experiment proves conclusively that the critical absorption lies between the emission lines  $\beta_2$  and  $\beta_5$ , in other words it has a longer wave-length than that of  $\beta_5$ .

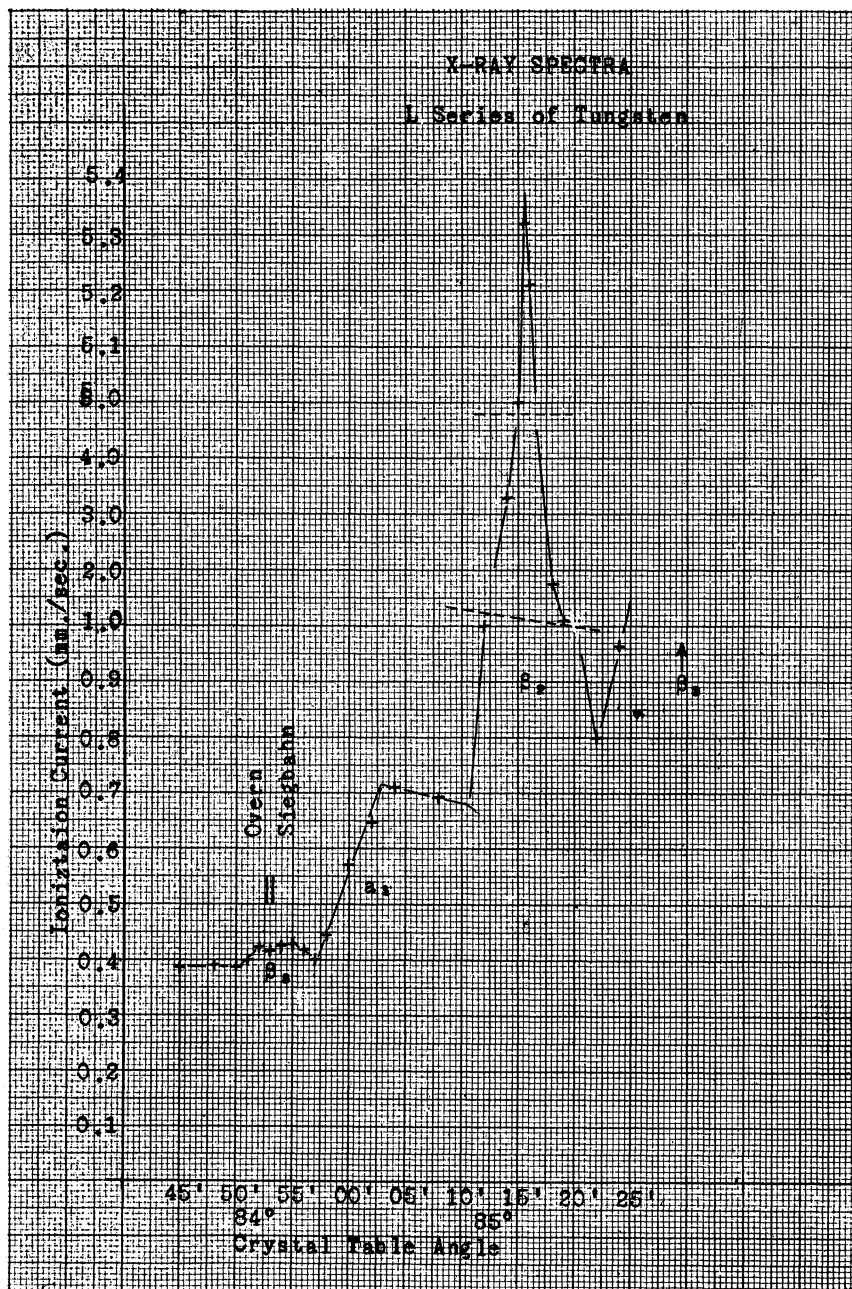


FIG. 1

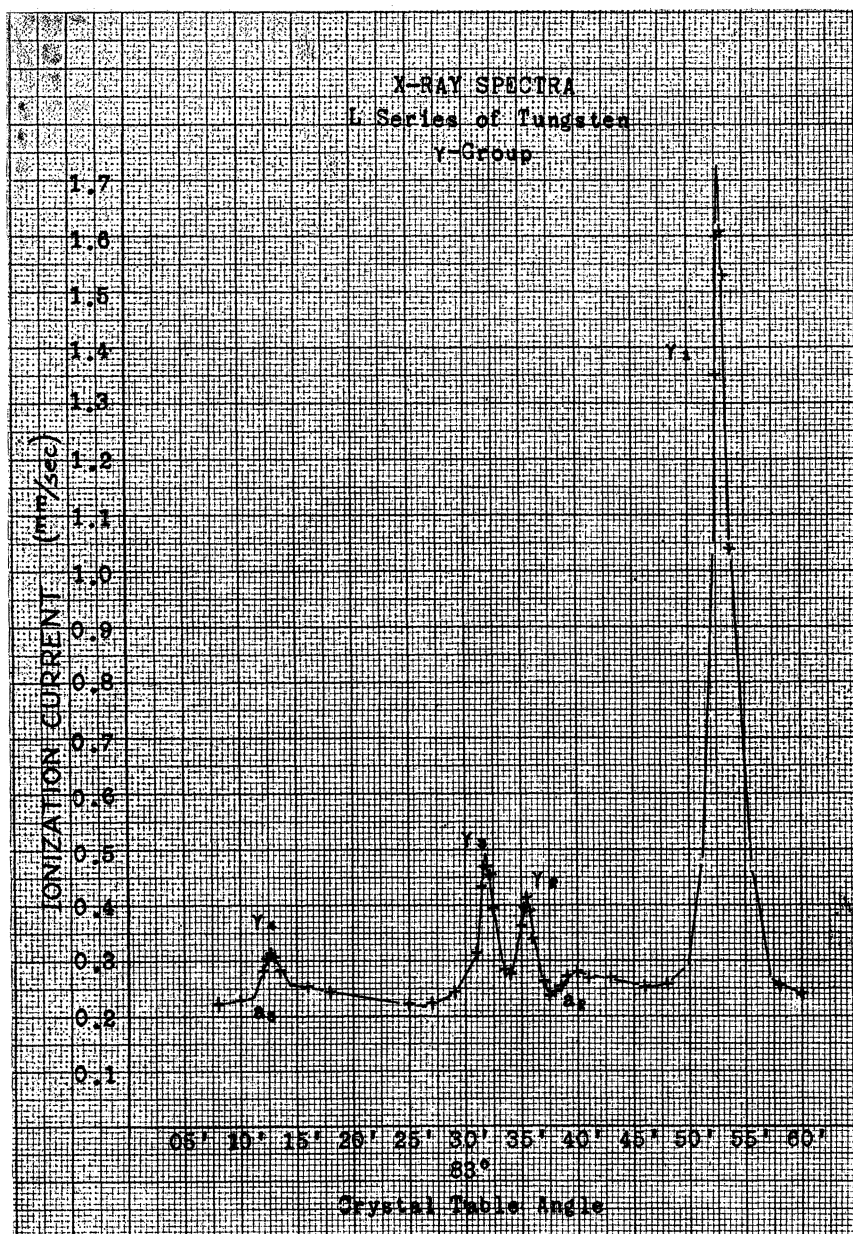


FIG. 2

The positions of  $\beta_5$  as determined from the measurements of Overn<sup>9</sup> and Siegbahn<sup>10</sup> are marked above the curve in figure 1. According to their measurements this faint line has a wave-length a small fraction of one per cent shorter than our value, which would bring it still further from the critical absorption in the direction of shorter wave-lengths.

The curve in figure 2 represents the spectrum of tungsten in the neighborhood of the critical absorption  $La_2$ . The drop corresponding to the absorption and the peaks corresponding to the  $\gamma$  emission lines appear on the curve. The critical absorption lies between the emission lines  $\gamma_1$  and  $\gamma_2$ , and therefore has a wave-length longer than that of  $\gamma_2$ . Overn's and Siegbahn's values for  $\gamma_2$  are in exact agreement with our values.

According to the conception of radiation held by many scientists the critical absorption wave-length corresponds to the short wave-length limit of the group or series of emission lines with which it is associated. If this be true, or, to speak more accurately, if the term "group of lines" is defined in such a way that this is true, then  $\beta_5$  cannot belong to the first group in the  $L$  series of X-rays, and  $\gamma_2$  cannot belong to the second group.

The strongest evidence in favor of believing that  $\beta_5$  belongs to the same *atomic mechanism* that produces the lines in the first group appears to be that the square root of its frequency increases from atom to atom nearly as a linear function of the atomic number, corresponding in this respect to all the lines in the first group but not to those in the second and third groups. In terms of the theory of atomic orbits this means that electrons falling into the  $L_1$  orbit produce the line  $\beta_5$ , as they do all the lines in group 1. Webster and Clark<sup>4</sup> found that  $\beta_5$  in the platinum spectrum appeared at a lower voltage than that required to produce the lines in the second group. This proves conclusively that  $\beta_5$  cannot belong to the second group. The experiments on critical potentials, however, are not sufficiently accurate to decide whether  $\beta_5$  appears at *exactly* the same voltage as the other lines in group 1, for  $\beta_5$  is a weak line, and the difference between its wave-length and that of the critical absorption  $L_1$  amounts to only 0.7% for tungsten. We are not, therefore, compelled to assume that  $\beta_5$  can be produced by electrons in the X-ray tube having quantities of energy less than that given by the quantum equation,  $Ve = h\nu$ .

The argument in favor of supposing that the line  $\gamma_2$  belongs to the mechanism that produces the lines in the second group rests largely upon the fact that for the various chemical elements the difference in frequency between  $\gamma_2$  and  $\beta_5$  equals the frequency interval between the lines in the other pairs belonging respectively to the two groups. It also equals the difference in frequency between the two critical absorptions  $La_2$  and  $La_1$ , and is given quite accurately by Sommerfeld's  $L$  doublet formula. Hence, according to the theory of electron orbits,  $\gamma_2$ , in common with the

other lines belonging to the second group, is produced by electrons falling into the second,  $L_2$ , orbit.

On the experimental and theoretical evidence we have reached the conclusion that the emission line  $\beta_5$  belongs to the atomic mechanism that produces the lines in the  $L_1$  group, and that  $\gamma_2$  belongs to that producing the lines in the  $L_2$  group. On the other hand our experiments prove conclusively that the wave-length of  $\beta_5$  is shorter than that of the  $La_1$  critical absorption, and that the wave-length of  $\gamma_2$  is shorter than that of  $La_2$ . A somewhat similar situation occurs in the spectra of ordinary light. Here we have resonance and ionization potentials. There is a difference, however, between the character of the absorption of X-rays and that of ordinary light.

The best way of explaining these phenomena may be somewhat as follows: Let us suppose that the critical absorption  $La_1$  corresponds to the transfer of an electron from the  $L_1$  orbit to the periphery of the atom—to an orbit there where it can find a place to stick. This does not mean a transfer to an indefinitely great distance from the centre of the atom. There may be many orbits outside that at the periphery, even in addition to those that belong to visible spectra. With the electron in the orbit at the periphery the atom is in a state such that by the transfer of an electron back to fill the vacancy in the  $L_1$  orbit it can radiate any one of the emission lines  $1, \alpha_2, \alpha_1, \beta_2$ , etc., but not  $\beta_5$ . If, now, the frequency of the incident X-ray beam is higher than that of the critical absorption, if the energy  $h\nu$  is greater than that required to lift the electron to the periphery of the atom, it may carry the electron to an orbit further out or even outside of the atom altogether. In this case the atom would be in a state such that the return of an electron from one of these outside orbits would emit X-radiation of higher frequency and shorter wave-length than that of the critical absorption. This would correspond to the emission line  $\beta_5$ . A similar explanation applies also to the emission line  $\gamma_2$ , and the  $L_2$  orbit.

From this point of view we would expect the critical potential for  $\beta_5$  to be slightly higher than that for the other lines belonging to the  $L_1$  orbit, and the critical potential for  $\gamma_2$  to be slightly higher than that for the lines associated with the  $L_2$  orbit.

Further, on this theory, the critical absorption does not correspond to the limit of the group, or series. It becomes incorrect to speak of the "absorption limit," as these words are usually employed.

An accurate, quantitative test for our point of view cannot be obtained without making special assumptions. According to our measurements, however, the difference in frequency between the emission line and the critical absorption for tungsten, each divided by the Rydberg constant, is 6.0 for  $\beta_5-La_1$ , and 5.6 for  $\gamma_2-La_2$ . These are of the order of magnitude of frequencies associated with the peripheries of atoms.



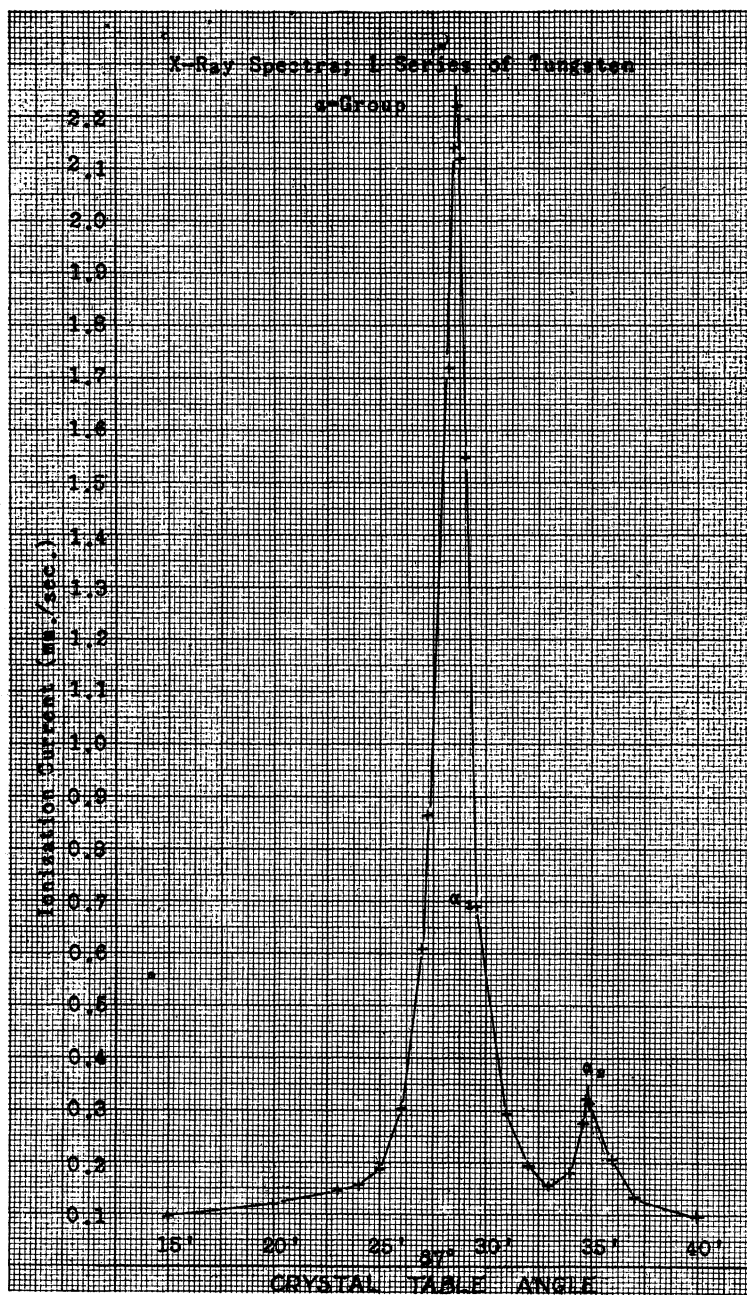


FIG. 3

The question now arises as to whether or not an  $L$  critical ionization frequency equals an  $L$  critical absorption frequency. A critical ionization frequency represents the transfer of an electron completely *outside* of an atom. In the case of the  $K$  series of iodine the two frequencies have been found to be equal to each other within the limits of error of the measurements.<sup>7</sup> Experiments are in progress to test this point for the  $L$  series.

*Relative Intensities of Lines.*—The ionization spectrometer provides us with an excellent method of estimating the relative intensities of lines in X-ray spectra. Accurate estimates of the relative intensities, however, cannot be obtained unless the lines lie fairly close together. If a considerable interval separates them, corrections must be applied for the changes with varying wave-length in the amounts of energy absorbed by the substances through which the rays pass, etc. These corrections cannot be accurately calculated at present. Special precautions must be taken to make sure that no critical absorption nor critical ionization wave-length lies between the wave-length of the lines to be compared with each other. These limits to the accuracy of relative intensity measurements present themselves in photographic spectrometry in addition to those due to the difficulty of estimating the blackening of the photographic plates.

In the case of a line that is not perceptibly broadened we take the height of the peak corresponding to it on the ionization current crystal table angle graph to represent its intensity. This height must be measured from the level of the curve corresponding to the general radiation on the two sides of the peak, and not from the axis of zero ionization current.

Two peaks appear on the curve in figure 1, corresponding to the spectral lines  $\beta_2$  and  $\beta_5$ . The ratio of the heights of these two peaks is 116. This number, however, does not represent accurately the relative intensity of  $\beta_2$  to  $\beta_5$ , for the critical absorption of  $La_1$  lies between the two emission lines. The target absorbs a greater fraction of the X-ray energy in the neighborhood of  $\beta_5$  than it does in the neighborhood of  $\beta_2$ . In this case, therefore, the ratio of the heights of the peaks gives us only an upper limit for the ratio of the intensities.  $\beta_2$  cannot be more than 116 times as intense as  $\beta_5$ .

The curve in figure 2 contains four peaks corresponding to the emission lines  $\gamma_1$ ,  $\gamma_2$ ,  $\gamma_3$  and  $\gamma_4$ . The relative heights of these peaks are represented by the numbers 100, 14, 18 and 6. These numbers have not been corrected for the errors due to absorption, etc., so that they give only an approximate estimate of the relative intensities of the emission lines. The lines  $\gamma_2$  and  $\gamma_3$ , however, lie very close together, and the correction must be very small. Since the critical voltages for all the  $\gamma$  lines are not quite the same, their relative intensities depend somewhat on the voltage

applied to the X-ray tube. This was 22,750 volts. The applied voltage lies so far above the critical voltages, however, that the effect due to variations in the latter do not amount to as much as three per cent.

Figure 2 in the paper referred to above<sup>6</sup> contains curves representing the four strongest  $\beta$  lines. The heights of the peaks corresponding to  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$  and  $\beta_4$  are proportional respectively to the numbers 100, 55, 16 and 9; the voltage applied to the tube in this experiment being 24,800 volts.

The ratio of intensities of the two  $\alpha$  emission lines possesses special theoretical interest. Sommerfeld<sup>5</sup> has developed a theory which predicts the relative intensity of certain lines in the spectrum. By applying the quantum theory to electron orbits that do not lie in the same plane he finds that the number of positions which the plane of an orbit can occupy is greater by unity than the quantum number associated with the electron's angular coördinate. According to a line of reasoning due to Bohr<sup>11</sup> one of these positions is in a certain sense dynamically impossible, which reduces the number of possible positions the plane of the orbit can occupy by unity. According to Sommerfeld's theory all the possible positions of the orbit's plane are equally probably, and hence the intensity of the line is proportional to the number of possible positions.

In the case of the  $\alpha$  lines in the  $K$  series this theory agrees very well with the facts.<sup>8</sup> The  $\alpha$  lines in the  $L$  series, however, do not have the relative intensity predicted by the theory. The electrons producing these  $\alpha$  lines fall from  $M$  orbits into the same  $L_1$  orbit. Those producing the  $\alpha_1$  line fall from the first,  $M_1$ , orbit, which has three quanta associated with the angular coördinates, while those producing the  $\alpha_2$  line come from the orbit  $M_2$ , which has only two quanta associated with the angular coördinates. According to Sommerfeld, therefore, the relative intensities should be in the ratio of 4 to 3. As a matter of fact, the ratio is very much larger than this. The curve in figure 3 represents the two  $\alpha$  lines in the  $L$  series of tungsten. The ratio of the heights of the two peaks is about 10 to 1. According to Bohr's "analogue principle" the transfer from  $M_2$  to  $L_1$  could not take place, unless the atom were in a field of force. This may account for the weakness of the  $\alpha_2$  line.

<sup>1</sup> Siegbahn and Friman, *Phil. Mag.*, London, April, 1916 (403); and Nov. 1916 (497).

<sup>2</sup> de Broglie, *J. Physique*, Paris, May-June, 1916 (161).

<sup>3</sup> Duane and Patterson, *Proc. Nat. Acad. Sci.*, Washington, Sept. 1920.

<sup>4</sup> Webster and Clark, *Ibid.*, March, 1916; and Webster, *Ibid.*, Jan., 1920.

<sup>5</sup> Sommerfeld, *Atombau und Spektrallinien*.

<sup>6</sup> Duane and Patterson, *Physic. Rev.*, Ithaca, 1920.

<sup>7</sup> Duane and Hu, *Ibid.*, Oct., 1919 (369).

<sup>8</sup> Duane and Stenström, *Ibid.*, April, 1920 (329); and *Proc. Nat. Acad. Sci. Washington*, Aug., 1920.

<sup>9</sup> Overn, *Physic. Rev.*, Aug., 1919 (137).

<sup>10</sup> Siegbahn, *Phil. Mag.*, Nov., 1919 (639).

<sup>11</sup> Bohr, *Copenhagen Academy*, 1918.